High-Efficiency Heterojunction Photovoltaic Devices by Block Copolymer Nanotemplates.
(AOARD-04-4066)

Principal Investigator: Jin Kon Kim

Departments of Chemical Engineering,

Pohang University of Science and Technology,

Kyungbuk 790-784, Korea

Research Assistants

Jeong In Lee, Jeong A Jang, Unyong Jeong

Departments of Chemical Engineering,

Pohang University of Science and Technology,

Kyungbuk 790-784, Korea

Periods: 2004/09 ~ 2005/08

Report Documentation Page

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **27 JUL 2006**	2. REPORT TYPE	3. DATES COVERED

4. TITLE AND SUBTITLE **High-Efficiency Heterojunction Photovoltaic Devices by Block Copolymer Nanotemplates**	5a. CONTRACT NUMBER **FA520904P0403**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Kon Jin Kim**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Pohang Univeristy of Science and Technology,San 31, Hyo-ja Dong,Pohang 790-784,NA,Korea (Sou**	8. PERFORMING ORGANIZATION REPORT NUMBER **FA520904P0403**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Ultra high density arrays of conducting poly(pyrrole) (Ppy) and poly (3-hexyl thiopene) (P3HT) nanowires with diameters of 10~25 nm were prepared on indium-tin oxide coated glasses (ITO) by electropolymerization of the monomers inside nanoporous templated prepared by block copolymers. These high density arrays of conducting polymer nanowires could be used as P-type materials for photovoltaic devices. It was observed that even after the PS matrix was removed, the free standing conducting polymer nanowires persisted without collapsing the wire onto the substrate. Such structures could not be achieved by the electropolymerization of a conducting polymer inside an anodized aluminum oxide (AAO) membrane, where the nanowires were found to fall onto the substrate after the AAO was removed. After removal of the PS matrix, the HOMO and LUMO levels of Ppy nanowires were measured to be ? 4.93eV and -3.69eV, respectively, which are slightly larger than the corresponding values (-4.79eV and -3.43eV) for Ppy thin films prepared by electropolymerization. Since the energy level of ITO glass is-4.8 eV, Ppy nanowires are more suitable for use as a P-type material. Due to the free standing geometry, a second N-type polymer can be easily spin-coated onto this array. Such arrays of polymer nanowires were also prepared on ITO-coated poly (ethylene terepthalate) film; demonstrating a new pathway to flexible photovoltaic devices.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**		**23**	

Table of Contents

Abstract

Ulta high density arrays of conducting poly(pyrrole) (Ppy) and poly(3-hexyl thiopene) (P3HT) nanowires with diameters of 10 ~ 25 nm were prepared on indium-tin oxide coated glasses (ITO) by electropolymerization of the monomers inside nanoporous templated prepared by block copolymers. These high density arrays of conducting polymer nanowires could be used as P-type materials for photovoltaic devices. We found that even after the PS maxtrix was removed, the free standing conducting polymer nanowires persisted without collapsing the wires onto the substrate. Such structures could not be achieved by the electropolymerization of a conducting polymer inside an anodized alminium oxide (AAO)membrane, where the nanowires were found to fall onto the substrate after the AAO was removed. After removal of the PS matrix, the HOMO and LUMO levels of Ppy nanowires were measured to be –4.93eV and –3.69eV, respectively, which are slightly larger than the corresponding values (–4.79eV and –3.43eV) for Ppy thin films prepared by electropolymerization. Since the energy level of ITO glass is – 4.8 eV, Ppy nanowires are more suitable for use as a P-type material. Due to the free-standing geometry, a second N-type polymer can be easily spin-coated onto this array. Such arrays of polymer nanowires were also prepaerd on ITO-coated poly(ethylene terephthalate) film; demonstrating a new pathway to flexible photovolatic devices.

1. Introduction

Nanoporous templates have been used for the fabrication of nanostructured materials having their potential applications in electronics, optics, magnetism, energy storage, and electrochemical deposition. Both particle track-etched polymer membranes and the anodized aluminum oxide (AAO) membrane have been widely used. The former contains randomly distributed nanochannels and pore densities of ~ 10^9 pores/cm^2.[1~5] Martin and coworkers synthesized conducting polymer fibers by using commercial particle track-etched polycarbonate membrane.[6] But, due to relatively low porosities (10^5 ~ 10^9 pores/cm^2), high densities of nanowires of conducting polymers could not be achieved.

Anodized alumina membranes have been widely employed to fabricate nanowires, templates for protein separation, and the preparation of carbon nanotube.[7~9] Recently, well-defined nanotube arrays of poly(3,4-ethylenedioxythiopene) (PEDOT) have been prepared by electrochemical polymerization of the monomer these membranes.[10] However, the orientation of nanotubes (or nanowires) normal to the substrate is lost since the configuration of the nanotubes is unstable upon removal of the AAO and they collapse onto the substrate.

There have been extensive studies on photovoltaic devices based on organic and polymeric PN heterojunction materials because of easy processability, low cost of fabrication, and flexible properties. However, the power conversion efficiency (η_p) of these devices is only ~2 %, [11] much less (~ 24 %) with crystalline silicone and ~17 % with thin film silicone.[12] The main reason is that free electrons and holes are not directly produced by photon absorption in the organic or polymer materials. Rather the electron-hole pairs (excitons) are created, and dissociated into holes and electrons. The dissociation of excitons in the heterojunction photovoltaic (PV) devices occurs mainly at the interface of the hole (P type conducting polymer) and electron acceptor (N type conducting polymer).[13,14] Two different PN-heterojunction PV device geometries are reported: bilayer laminated films of P type/N type conducting polymers[11], and single-layered film where P type/N type conducting polymers phase separate into

2

bicontinuous interpenetrating network (IPN) structures,[15,16] as shown in Figure 1.   Although the P-N contact area of the heterojunction for the single-layered IPN structures is much larger than that with bilayerd geometry, the holes and electrons transport to the collection electrodes for the IPN structures is much less, since some electrons cannot cross the hole acceptor barrier unless all of the electron-acceptor domains are connected to the electrode. The maximum diffusion length for excitons before their disappearance is ~ 20 nm; therefore the distance between P-type and N-type materials should be less than 20 nm.   Also, all of hole- and electron- acceptors domains should make contact to their respective electrodes (ITO coated glass for holes and aluminum for electrons).

We found that the block copolymer nanoporous template made of polystyrene-*block*-poly(methyl methacrylate) (PS-b-PMMA) can satisfy the above two criterions, as shown in Figure 1(c).   Previous studies have shown that arrays of nanoscopic cylindrical microdomains oriented normal to the surface of the film can easily prepared.[17-20]   By removal of one of the components of PS-b-PMMA or of added homopolymer, nanoporous films are produced with areal pore densities similar to that of AAO membranes.   Not only can the templates be prepared on rigid supports but they could be prepared on flexible substrates.   In addition, upon removal of the matrix polymer, the special configuration of the nanowires was preserved, which is a necessary step for the introduction of another N type material by spin-coating.

Here we show the use of block copolymer templates to fabricate high-efficiency PV devices.   After the removal of the PS matrix, the HOMO and LUMO level of Ppy or P3HT were essentially the same as those of the pure polymers.   Since the N-type material can easily be spin-coated onto this array, this technique is easily employed for preparing a new type of photovolatic devices with high conversion efficiency.

2. Experimental

2.1 Materials

An asymmetric PS-b-PMMA, having a styrene weight fraction of 0.70 and a weight average molecular weight (M_w) of 66,000 with a polydispersity of 1.19, was prepared by ATRP (Atom Transfer Radical Polymerization).[20] PMMA homopolymer with M_w = 31,800 and a polydispersity of 1.08 (Polymer Source Inc.) was used as received. A hydroxy terminated random copolymer of styrene and methyl methacrylate, denoted PS-*r*-PMMA, having a styrene weight fraction of 0.58 and M_w of 11,000 with polydispersity of 1.13, was anchored to the substrate and balance interfacial interaction so as to orient the PMMA microdomains normal to the substrate. PEDOT (poly 3, 4-ethylenedioxythiopene) used as protective layer was purchased from Dow Chemical. For polypyrrole polymerization, 99% pyrrole monomer (C_4H_5N, Acros) was vacuum distilled prior to use. Lithium perchlorate ($LiClO_4$, Aldrich) was added as a dopant and propylene carbonate (Acros) was used as an electrolyte solvent.

2.2. Preparation of Nano Porous Templates

Figure 2 gives a schematic of the fabrication of PV device by using block copolymer templates. Here, (1) a nanoporous template was produced using thin films of PS-b-PMMA on PEDOT-coated ITO glass. (2) Pyrrole or 3-hexyl thiopene as P-type conducting polymer nanowires were polymerized within the nanopores in the template by an electrochemical polymerization to produce nanowires in a PS matrix. (3) The PS was removed, and an N-type conducting polymer was spin-coated onto the substrate with the nanowires. (4) An aluminum electrode was vapor-deposited on top of this as the second electrode.

ITO glass was first cleaned by using mixture solvents of chloroform, isopropyl alcohol and acetone for 30 minutes, sonicated for 15 min in 1:1 isopropyl alcohol and acetone solution, and finally, rinsed with deionized water. The cleaned ITO coated glass was treated with O_2 plasma to remove any trace of organic materials, and the surface of ITO was flattened for 15 min

with a microwave-generated plasma reactor. (Plasmatic Systems Inc., PLASMATIC-PREENII, 24. GHz)   Then, PEDOT (poly 3,4-ethylene dioxythiopene) solution was spin coated on the ITO glass and this layer was used as protective layer.

The block copolymer templates with thickness ranging from 30~ 300 nm were prepared by procedures established previously.[17-20]   To maintain the orientation of the microdomains normal to the substrate in films thicker than ~ 50 nm, PMMA homopolymer was added, as discussed previously.[20]

2.3. Fabrication and Observation of Nanowires

Polypyrrole (Ppy) was electrochemically polymerized at room temperature using 0.01 M pyrrole monomer in 0.001M lithium perchlorate in the propylene carbonate at 0.64 V.   The working electrode was ITO glass on which a block copolymer nanoporous template was fabricated.   A Pt was used as a counter electrode and an Ag/AgCl electrode was used as a reference electrode.   The oxidation potential of ferrocene against Ag/AgCl reference electrode was used as an internal standard of −4.82 eV.   Current change with time was recorded using a potentiostat controlled by PowerLab/4SP (ADInstruments).   PPy nanowires were grown from the bottom of ITO glass located at the bases of pores in the templates.   The potential and exposure time for electropolymerization was chosen to optimize the height (~ 100 nm) of Ppy nanowires.

The crosslinked PS matrix must be removed before spin-coating the N-type conducting polymer.   Since PS was crosslinked, it was removed by combustion at high temperature (~ 400 ºC) or by reactive ion etching (RIE).   For nanotemplates prepared using the mixture of PS-PMMA and PMMA homopolymer, PMMA homopolymer was selectively removed by washing with acetic acid.   In this case, the block copolymer matrix could be easily removed by toluene.

The size of nanoholes and polypyrrole nanowires were studied by using Scanning Force Microscope (SFM; Digital Instrument D3000) in the tapping mode with silicone nitride tips on cantilevers (Nanoprobe) with a spring constant ranging from 40.0~66.0N/m, and with Field

Emission Scanning Electron Microscopy (FE-SEM : Hitachi S-4200) operating at 120 kV. The cross-sectional images of nanowires were obtained with FE-SEM having a focused ion beam (FIB).   The sample was first coated with Pt, slanted at an angle of 52 ^{o}, and finally cut by using a FIB (FEI Co., NOVA200).

The energy level for the highest occupied molecular orbital (HOMO) was measured in the cyclic voltamograms (CV) obtained by a potentiostat with a voltage sweep apparatus.   The solution of 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile was used as an electrolyte solution and the first oxidation point was taken as the HOMO value.   The oxidation potential of ferrocene against Ag/AgCl reference electrode was used as an internal standard of -4.82 eV. The energy level for the lowest unoccupied molecular orbital (LUMO) value was determined from the band gap between the absorption band edge in the UV-Vis spectrum and the HOMO value.

3. Results and Discussion

Figure 3(a) shows an FE-SEM image of a nanoporous block copolymer template on ITO glass, with cylindrical pores oriented normal to the substrate.   From the cross-sectional SEM image (Figure 3(c)), the pores are seen to span the entire film thickness.   Figure 3(b) shows an AFM height image of a nanoporous template on a Ppy-coated ITO glass.   A similar structure was observed on PEDOT layer.

Figure 4 is typical CV (Cyclic voltammogram) which represents the plot of current versus voltage) during electrochemical polymerization of pyrrole on the ITO glass without having a nanoporous template. This curve is useful to check the oxidation potential of pyrrole monomer.   Without pyrrole in an electrolyte, the current did not change as shown in the dotted line.   When 0.01M pyrrole was eletropolymerized in an electrolyte of 0.001M LiClO$_4$ in propylene carbonate solution, it showed typical curve of the oxidation and reduction of pyrrole. From Figure 4, we obtained the oxidation potential of pyrrole of ~ 0.7 V.   This potential was measured by the starting point of oxidation peak.   This suggests that the electrochemical

polymerization of pyrrole was successful in the above condition.

Figure 5 is the CV during electropolymerization of pyrrole inside the nano porous template. The shape of the CV of polypyrrole growth inside nano porous templates is almost same as that on ITO glass. Therefore, we can confirm that polypyrrole nanowires grown inside the template have same property as bulk polypyrrole prepared by electropolymrization. It is possible that the monomer and dopant electrolyte are diffusible into the base film (in this case, the crosslinked PS) during electrochemical polymerization of conducting polymer at a higher potential. Figure 6 shows chromoamperogram (current versus eletropolymerization time) at a 0.64 V for pyrrole on two substrates: (1) PEDOT-coated ITO, and a thin layer of polystyrene (100 nm) was additional coated on PEDOT-coated ITO. It is seen that for PEDOT-coated ITO surface, oxidative pyrrole reaction occurs, but when an additional PS layer is coated, there is no electropolymerization of pyrrole. Therefore, we conclude that the electrochemical polymerization did not occur within the PS matrix at a 0.64 V; thus we chose this potential for the growth of polypyrrole nanowires.

Figure 7(a) gives the characteristic chromo-amperogam at 0.64V during the electropolymerization of pyrrole within the naoporoes. It is noted that the current-voltage characteristic was gradually changed with the extent of pore filling. However, when the pores were entirely filled with Ppy, and Ppy reached the top of the template, this characteristic was changed dramatically. Thus, the experiment should be carried out at short electropolymerization times, where only Ppy nanowires grow inside the nanoporous templates. The height of polypyrrole nanowires inside nano porous template at various electropolymerization times was qualitatively determined by the change of the peak intensity at ~ 580 nm of UV- vis spectroscopy.

The height of polypyrrole nanowires inside nano porous template increases with electropolymerization time, which is qualitatively observed by UV- vis spectroscopy, as shown in Figure 8(a). The intensity of the absorbance peak at ~ 580 nm corresponding to the polypyrrole increased linearly with increasing polymerization time up to 60 min, as shown in Figure 8(b). Interestingly, the absorbance peak of polypyrrole polymerized for 2 h was red-shift,

indicating that polypyrroles were over-grown.   From the result in Figure 8(b), the height of ppy nanowires was increased linearly with polymerization time, which is verified by cross-sectional SEM images of nanowires.

Figure 9 shows top-view FE-SEM images of PPy nanowires grown inside the nanoporous template for different electropolymerization times at 0.64 V.   Three different methods were used to remove the crosslinked PS matrix: (1): combustion of the matrix at 400 ℃; (2) the UV etching under the air; and (3) the reactive ion etching (RIE) with oxygen source.   We found that the morphologies of nanowires were the same irrespective methods used to remove the PS matrix. It is seen in Figure 9 that the height of PPy nanowires was uniform, and the diameters of nanowires were essentially the same as that of nanoporous templates.   Figure 10 shows height image of polypyrrole nanowires grown inside the nanoporous template for 30 min and a 0.64 V. The matrix of crosslinked PS phase was removed by the combustion at 400 ℃.   The height of the wires after electropolymerization for 30 min and 60 min was ~ 50 nm and ~ 80 nm, respectively.   The measured values of HOMO and LUMO for the Ppy nanowires were –4.93eV and –3.69eV, respectively, which are slightly larger than those (–4.79eV and –3.43eV) of thin Ppy films prepared by electropolymerization.   Since the energy level of ITO glass is – 4.8 eV, the Ppy nanowires are better suited as the P-type material.

A mild condition was also developed to remove the PS matrix by using block copolymer/homopolymer mixture.   Here, the diameter of nanopore was ~ 11 nm, as shown in Figure 11.   Since the PS-b-PMMA could be easily removed with toluene, the damage for Ppy nanowires during the removal of PS matrix by RIE or combustion was effectively prevented.

Finally, we also found that another P-type of polymer nanowires made of P3HT nanowires were successfully prepared by the block copolymer nanotemplate.   Since the HOMO and LUMO values are easily controlled by proper choice of a P-type polymer, an N-type such as MEH-PPV without or with C_{60} can be spin-coated.   The geometry given in Figure 1(c) would be a promising photovoltaic device with high efficient convergence.

Conclusion

Nanoporous template by using PS-b-PMMA block copolymer on the ITO glass were prepared having pores oriented normal to the surface with a high lateral density (~ 10^{11} pores/cm^2). Pyrrole monomer was electrochemically polymerized within this template in a LiClO4 in propylene carbonate solution. The oxidation potential of pyrrole monomer was determined from cyclic voltammetry (CV) and the growth of polypyrrole nanowires was verified by the current change in chromoamperogram with eletropolymerization time. The vertical alignment array of Ppy nanowires maintained even upon revoval of the PS matrix. These nanowires prepared using block copolymer nanoporous template have potential use for photovoltaic device.

References

[1] J. C. Hulteen, C. R. Martin, *J. Mater. Chem.* **1997**, *7*, 1075.

[2] C. J. Brumlik, V. P. Menon, C. R. Martin, *J. Mater. Res.* **1994**, *9*, 1174.

[3] C. R. Martin, *Science* **1994**, *266*, 1961.

[4] C. R. Martin, *Chem. Mater.* **1996**, *8*, 1739.

[5] S. M. Marinakos, L. C. Brousseau, III, A. Jones, D. L. Feldheim, *Chem. Mater.* **1998**, *10*, 1214.

[6] R. M. Penner, C. R. Martin, *J. Electrochem. Soc.* **1986**, *133*, 2206.

[7] W. Liang, C. R. Martin, *J. Am. Chem. Soc.* **1990**, *112*, 9666.

[8] C. J. Brumlik, C. R. Martin, *J. Am. Chem. Soc.* **1991**, *113*, 3174.

[9] G. Che, B. B. lakshmi, E. R. Fisher, C. R. Martin, *Nature*, **1998**, *393*, 346.

[10] S. I. Cho, W. J. Kwon, S, J. Choi, P. Kim, S. A. Park, J. Kim, S. J. Son, R. Xiao, S. H. Kim, S. B. Lee, *Adv. Mater.* **2005**, *17*, 171.

[11] M. Granstroem, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson, R. H. Friend, *Nature,* **1998**, *395*, 257.

[12] S. E. Shaheen, D. S, Ginley, G. E. Jabbour, *MRS Bull.*, **2005**, *30*, 10.

[13] C. J. Brabec, G. Zerza, G. Cerullo, S. De-Silvestris, S. Luzatti, J. C. Hummelen, S. Saricihtci, *Chem. Phys. Lett.* **2001**, *340*, 232.

[14] J. J. M. Halls, K. Pichler, R. H. Friend, S. C. Moratti, A. B. Holmes, *Appl. Phys. Lett.* **1996**, *68*, 3120.

[15] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature,* **1995**, *376*, 498.

[16] G. Yu, A. J. Heeger, *J. Appl. Phys.* **1995**, *78*, 4510.

[17] T. Thurn-Albrecht, J. Schotter, A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. uarini, C. T. Black, M. T. Tuominen,T. P. Russell, *Science* **2000**, *290*, 2126.

[18] T. Thurn-Albrecht, R. Steiner, J. DeRouchey, C. M. Stafford, E. Huang, M. Ball, M. Tuominen, C. J. Hawker, T. P. Russell, *Adv. Mater.* **2000**, *12*, 787.

[19] C. T. Black, K. W. Guarini, K. R. Milkove, S. M. Baker, M. T. Tuominen,T. P. Russell, *Appl. Phys. Lett.* **2001**, *79*, 409.

[20] U. Jeong, D. Y. Ryu, D. H. Kho, J. K. Kim, J. T. Goldbach, D. H. Kim, T. P. Russell, *Adv. Mater.* **2004**, *16*, 533.
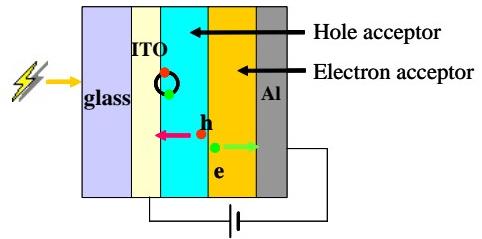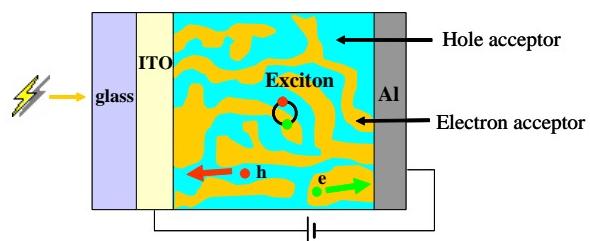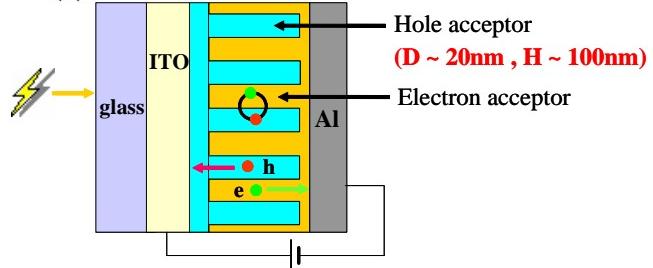
Figure 1. Various Configuration for photovoltaic Cell. (a) Bilayer Configuration, (b) Single Layer with IPN morphology, and (c) The best geometry for heterojunction
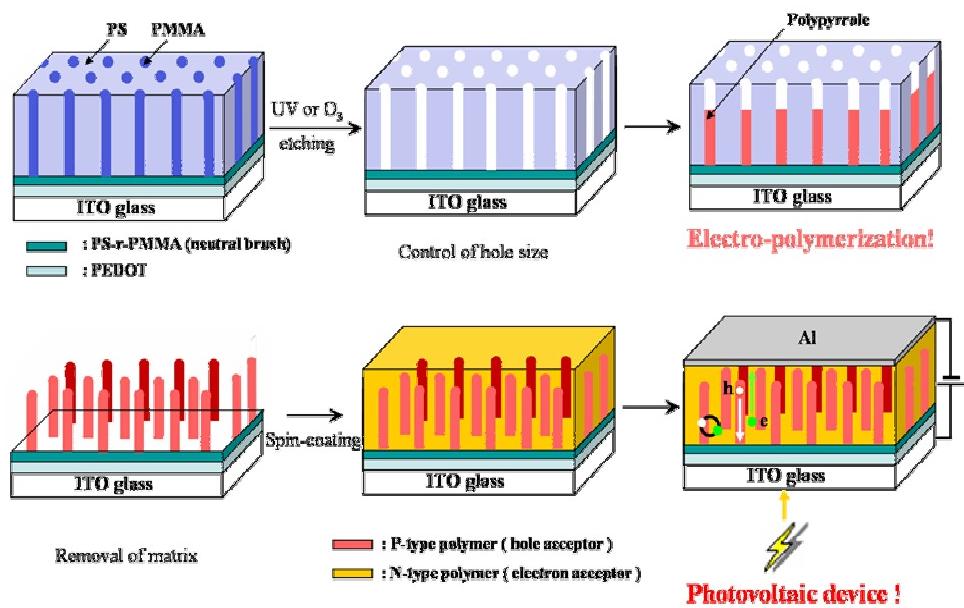
Figure 2. The procedure for the fabrication of photovoltaic devices from block copolymer nanoporous templates; (1) nano porous template was produced by PS-b-PMMA. (2) polypyrrole (P-type conducting polymer) nanowires were polymerized from pyrrole monomer inside the template by using electrochemical polymerization. (3) PS matrix was removed. (4) N-type conducting polymer was spin-coated.
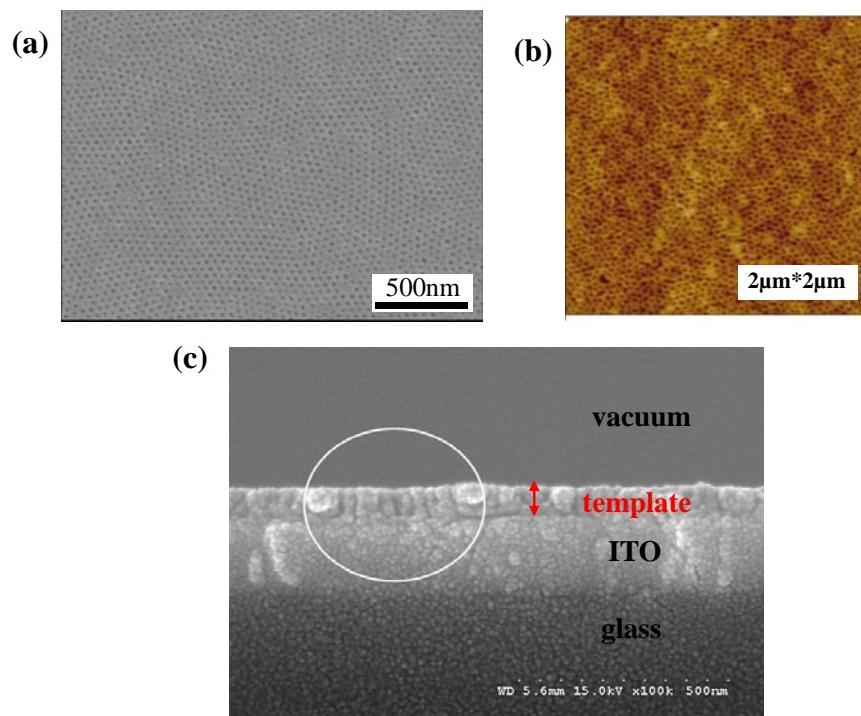
Figure 3. (a) FE-SEM image of nanoporous template prepared by PS-b-PMMA copolymer on ITO glass and (b) AFM image of nanoporous template prepared by PS-b-PMMA copolymer on a Ppy-coated ITO glass, and (c) the cross-sectional SEM image of nanoporous template of Figure 3(a).
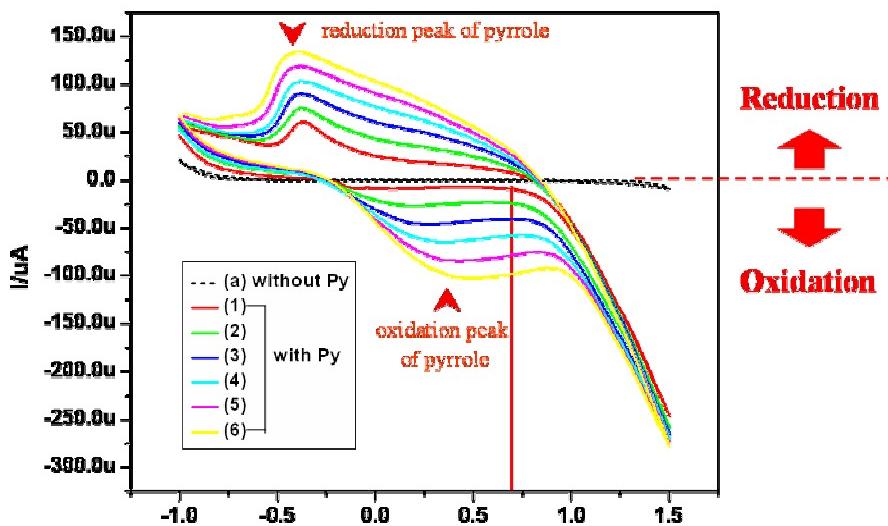
Figure 4. Cyclic voltammograms (CV) during electrochemical polymerization of pyrrole on the ITO glass without having a nanoporous template. (1) ~ (6) represent the cycle numbers of positive scan from -1.0 V to 1.5 V at a scan rate of 100 mV/s. The concentration of pyrrole was 0.01M pyrrole in an electrolyte of 0.001M LiClO$_4$ in propylene carbonate solution. For the reference, this plot without pyrrole was added as dotted line.
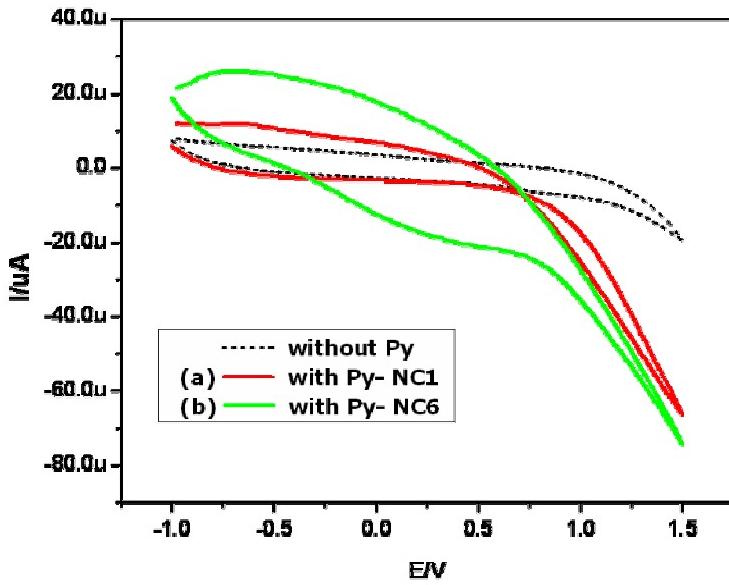
Figure 5. Cyclic voltammograms (CV) during electrochemical polymerization of pyrrole inside nanoporous template on the ITO glass on the ITO glass.   (a) and (b) represent the first and 6th cycles of positive scan from -1.0 V to 1.5 V at a scan rate of 100 mV/s.   The concentration of pyrrole was 0.01M pyrrole in an electrolyte of 0.001M LiClO$_4$ in propylene carbonate solution. For the reference, this plot without pyrrole was added as dotted line.
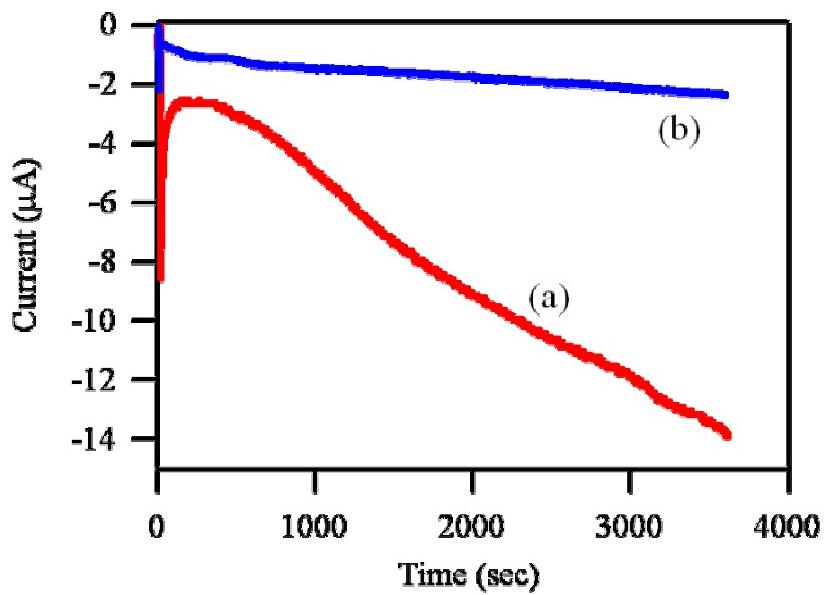
Figure 6. Current change with time (Chromoamperograms) at a 0.64 V during electropolymerization of 0.01M pyrrole and 0.001M LiClO$_4$ in propylene carbonate onto two substrates: (a) PEDOT-coated ITO, (b) an additional PS layer (100 nm) was coated onto PEDOT-coated ITO.
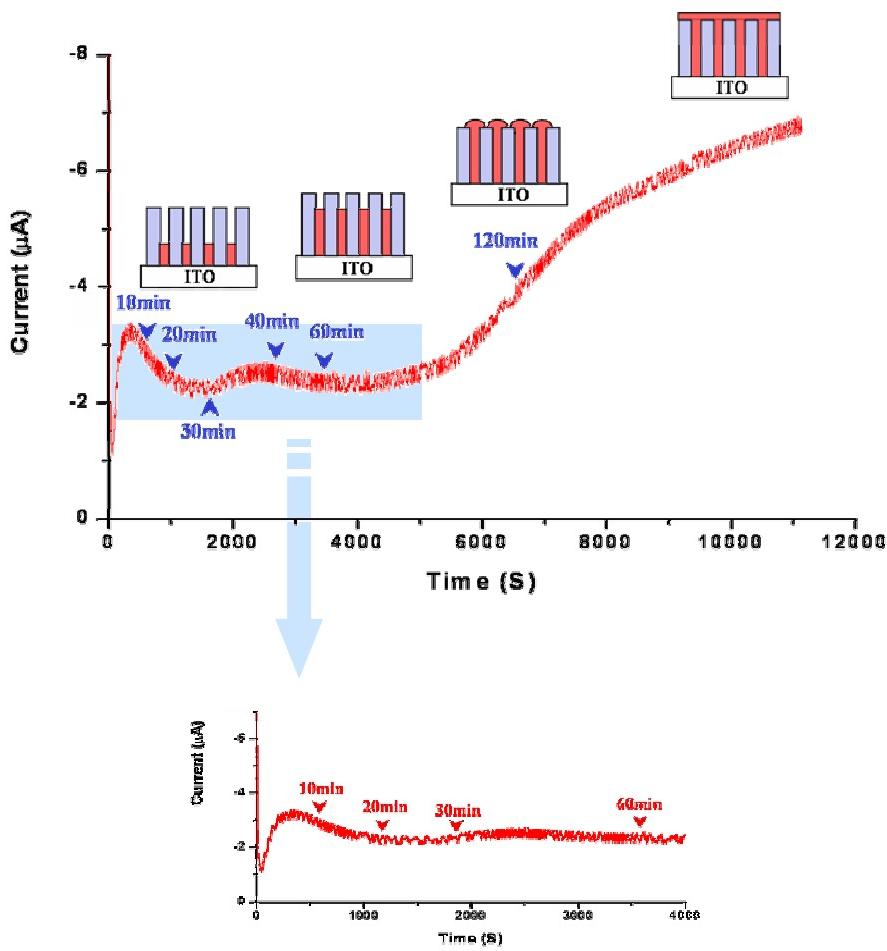
Figure 7. (a) Chromoamperogram of polypyrrole by electrochemical polymerization inside nanoporous template from 0.01M pyrrole and 0.001M LiClO$_4$ in propylene carbonate at a 0.64V
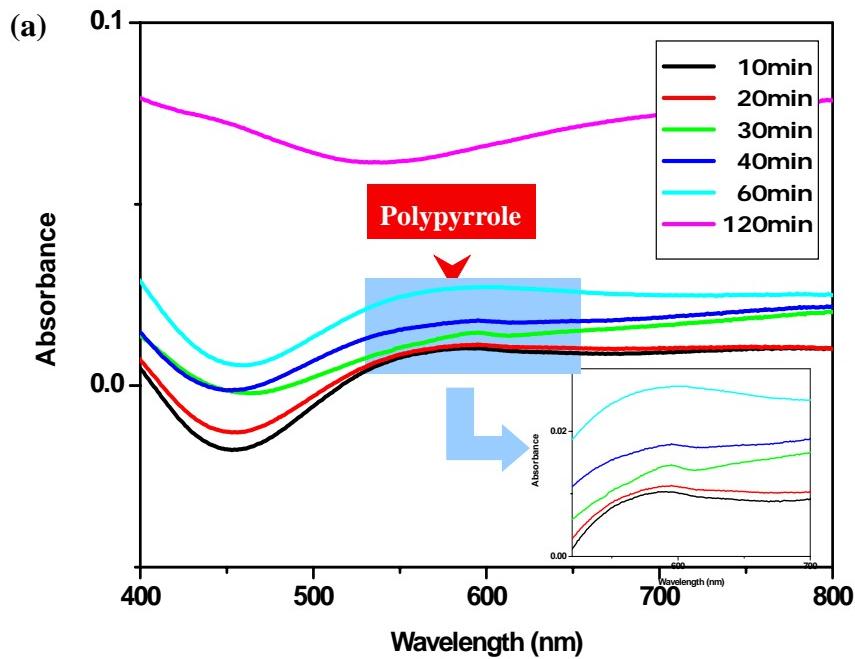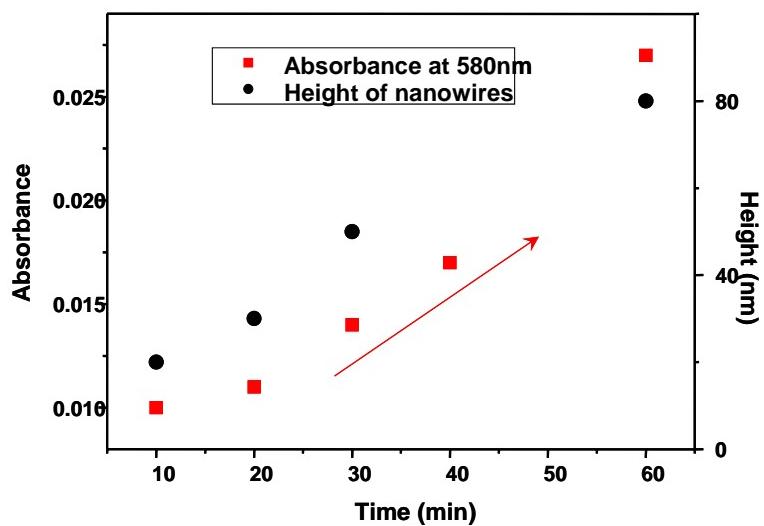
Figure 8. (a) UV-vis spectroscopy of polypyrrole nanowires with various heights; The heights were controlled by electropolymerization times (10 ~ 120 min) at a 0.64V. (b) Comparison of absorbance and height nanowires according to the electropolyemerization time.
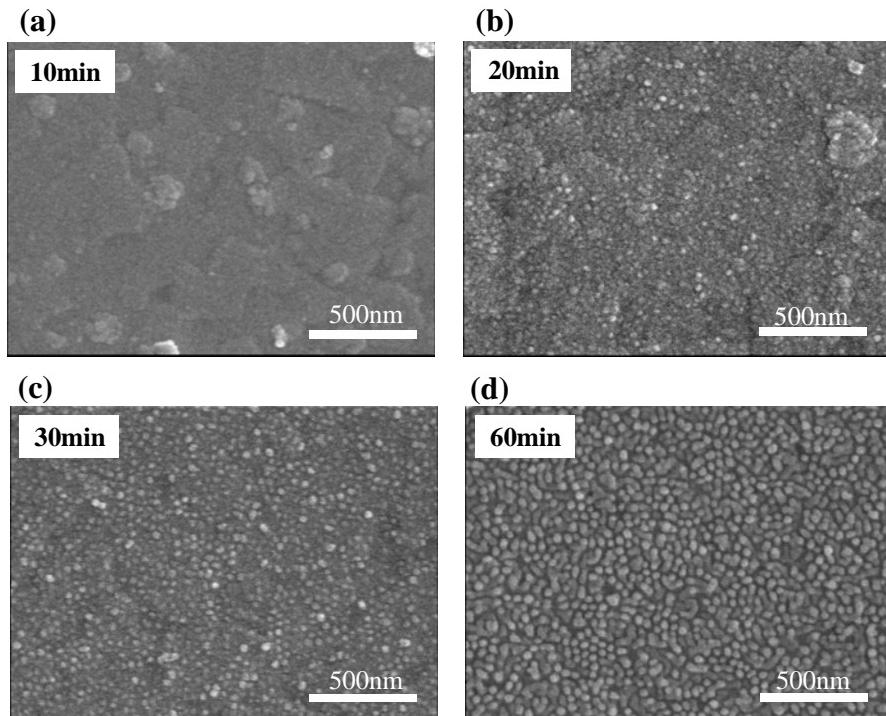
Figure 9. FE-SEM images of top view and cross-sectional view (insets) of the polypyrrole nanowires grown inside the nanoporous template at various electropolymerization times at a 0.64 V. (a) 10min, (b) 20min, (c) 30min and (d) 60min. The matrix of crosslinked PS phase was removed by combustion at 400 ℃.

(a) height ~ 50nm | 300nm | Pt | ITO | glass

(b) height ~ 80nm | 300nm | Pt | ITO | glass
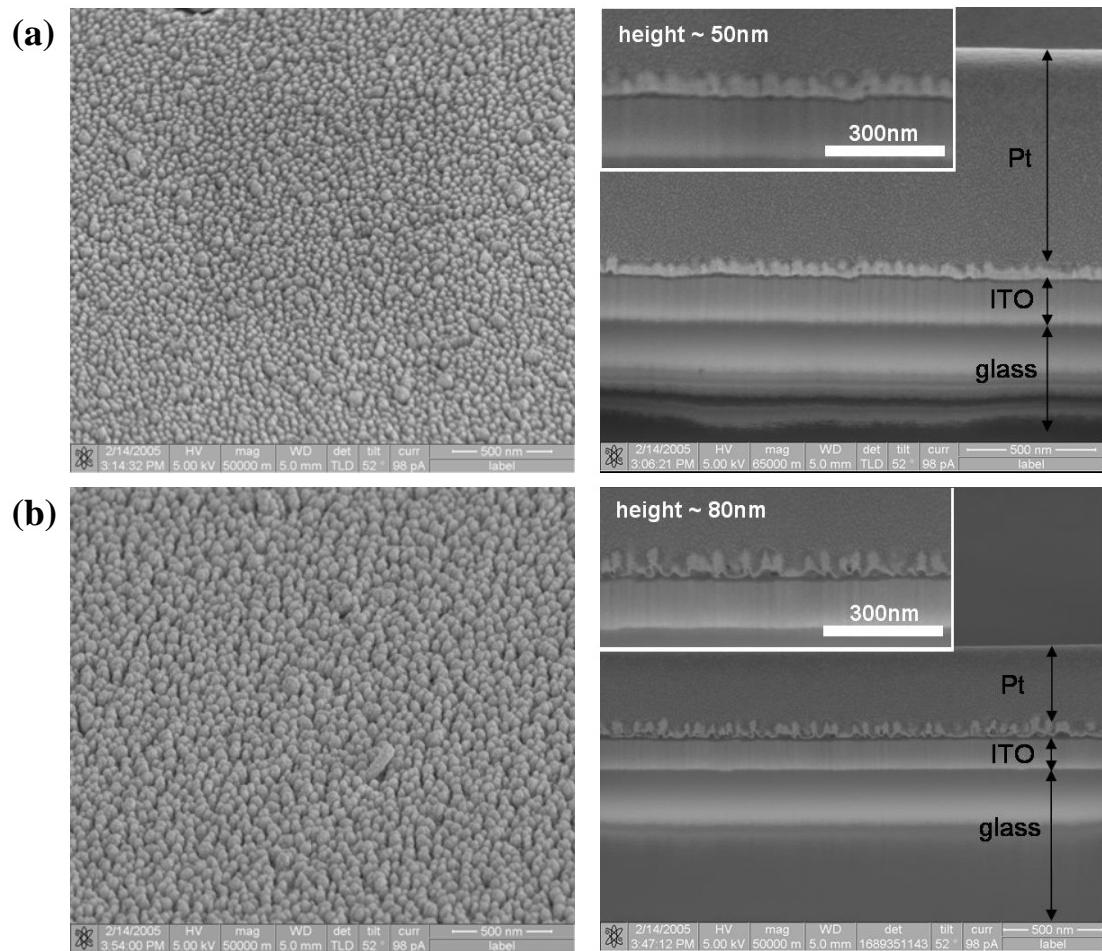
Figure 10. FIB (Focused Ion Beam) images of top view and cross-sectional view (insets) of the polypyrrole nanowires grown inside the nanoporous template at various electropolymerization times at a 0.64 V. (a) 30min, (b) 60min. The matrix of crosslinked PS phase was removed by combustion at 400 ℃.
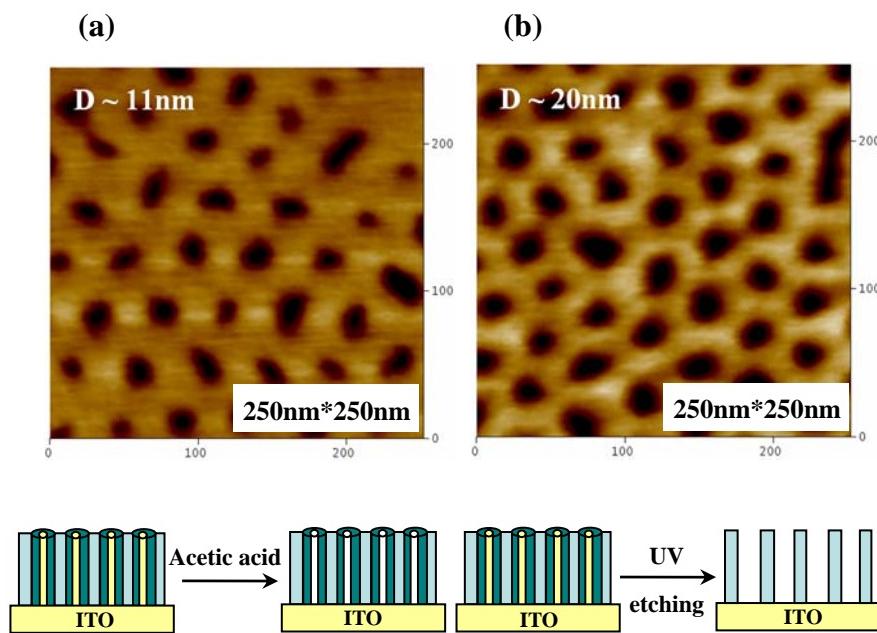
Figure 11. The AFM images of the top surface of the nanoporous template with different sizes of hole; (a) a template prepared by removing only PMMA homopolymer showed smaller holes having a diameter of ~ 11 nm, and (b) another template which was prepared by removing the entire PMMA phase (PMMA block plus PMMA homopolymer), showed large holes having a diameter of ~ 20 nm.